SOME ELECTROCHEMICAL AND THERMOCHEMICAL RELATIONS OF ZINC AND CADMIUM AMALGAMS.

By THEODORE WILLIAM RICHARDS AND GILBERT₄ NEWTON LEWIS.

INTRODUCTION.

THE nature of amalgams, although a matter of much interest, especially in the light of the modern theory of solutions, is still obscure. The subject has been studied from the standpoint of electrochemistry by several investigators, notably by Meyer, * who observed the electromotive forces of cells of the following type: — Dilute zinc amalgam of concentration x; Solution of zinc salt; Dilute zinc amalgam of concentration y. Since the total change in a cell of this kind consists in the transfer of metal between amalgams of different concentrations, the electrical energy obtained is equal to the maximum osmotic work obtainable by the process. On the assumption that the zinc in the dilute amalgam obeys the laws of dilute solution, Meyer derived the following expression : —

$$E = 1.908 \, \frac{q}{M} \, T \log \frac{c_1}{c_2};\qquad(1)$$

in which E represents electromotive force ; q, the electrochemical equivalent, in grams, of the metal carried in one second from one amalgam to the other; M, the molecular weight of the metal in the amalgam; T, the absolute temperature ; $\log \dfrac{c_1}{c_2}$, the common logarithm of the ratio of concentration of the amalgams. By comparing with this formula the experimental results, Meyer showed with sufficient exactness that in dilute amalgams the molecules of the metals studied by him are monatomic. If, on the other hand, the atomic weight is substituted for M in the formula, the agreement between the calculated and his observed electromotive forces is not close enough to show whether the dilute

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* Zeitschr. phys. Chem., VII. 477 (1891).

amalgams follow rigidly the laws of dilute solutions, on account of wide deviations in the observed values.

It has been the object of the present research to determine the electromotive forces of cells of the above type at varying temperatures, and with amalgams of all degrees of concentration, and also of similar cells in which one amalgam is replaced by the pure metal. Zinc and cadmium as metals, and normal solutions of their sulphates as electrolytes, were chosen as best adapted to the purpose. The experimental results were studied in relation to the two following equations: —

$$E = \frac{R}{ne_0} \, T \ln \frac{c_1}{c_2} = .000099 \; T \log \frac{c_1}{c_2}. \qquad (2)$$

$$\frac{dE}{dT} = \frac{E}{T} - \frac{Q}{ne_0 T}. \qquad (3)$$

Equation (2) is the simpler form that (1) assumes when the atomic weight is substituted for M. E is the observed electromotive force; R is the gas constant; n, the valence of the metal in question ($n = 2$ in the case of zinc and cadmium); e_0 is the quantity of electricity in coulombs which is carried by one gram-equivalent; $\ln \frac{c_1}{c_2}$ is the natural logarithm of the concentration ratio. A comparison of this formula with the experimental results shows the extent of applicability of the laws of dilute solutions to amalgams (assuming the molecule of the metal to be monatomic when amalgamated).

Equation (3) is the Helmholtz equation for the temperature coefficient of a cell, where Q is the heat given off by the cell during a transfer of n gram-equivalents. In the cells under consideration the only change produced by the current is the transfer of metal from the solid electrode to the amalgam, or from one amalgam to another more dilute. Q then represents either the heat of amalgamation of n gram-equivalents (one gram-atom) of the metal, or the heat of dilution of an amalgam containing one gram-atom. The use of this equation permits the calculation of these quantities from the temperature coefficient of the cell.[*]

Since the heat capacity of the amalgam is approximately the sum of the heat capacities of its constituents, the heat of amalgamation is practically constant. If we place a constant, h, in place of $\frac{Q}{ne_0}$, equation (3) becomes

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[*] Compare the interesting paper by Bugarszky, Zeit. anorg. Chem., XIV. 145.

$$\frac{dE}{dT} = \frac{E-h}{T}, \text{ or } \frac{dE}{E-h} = \frac{dT}{T},$$

integrating, $ln\,(E-h) = ln\,T + C = ln\,KT,$

where C is the integration constant and $C = ln\,K$, hence

$$E = KT + h. \tag{4}$$

Upon comparing this result with equation (3), which can be written $E = \frac{dE}{dT}T + \frac{Q}{ne_0}$, one sees that the outcome of this reasoning is simply the proof that if Q is constant $\frac{dE}{dT}$ (the temperature coefficient of the electromotive force) is also a constant. Thus the electromotive force of any cell of this type should be a linear function of the temperature.

MATERIALS AND APPARATUS.

The materials used in this research were of known purity. The mercury had been twice distilled *in vacuo*. The zinc and cadmium were prepared by electrolysis from chemically pure salts. The zinc sulphate had been prepared in this laboratory for atomic weight investigation. The cadmium sulphate was prepared by dissolving the electrolyzed metal in pure sulphuric acid, and crystallizing twice in order to free it from the excess of acid. The amalgams were prepared by mixing weighed amounts of mercury and the metal used and diluting as desired. The amalgams were weighed and kept under solutions of their sulphates to prevent oxidation.

Both cadmium and zinc, when electrolyzed from ammoniacal solutions of their sulphates, separate in tree-like forms, varying according to the conditions of electrolysis from large and distinct crystals to finely divided spongy masses. The latter form is produced by the stronger currents and greater dilutions.

The metal thus made, after suitable washing, was sometimes dried with alcohol and ether and converted into amalgam, or sometimes used at once in the pure state in the trial cells. The method of using this spongy material as an electrode is described later, on page 90.

The vessels in which the measurements were made consisted of large H tubes, with their lower extremities drawn out and turned upwards. Platinum wires run in through these fine tubes established the connection with the galvanometer. It was occasionally convenient to use a double H tube, in which one electrode could be connected through the same electrolyte with either of two electrodes.
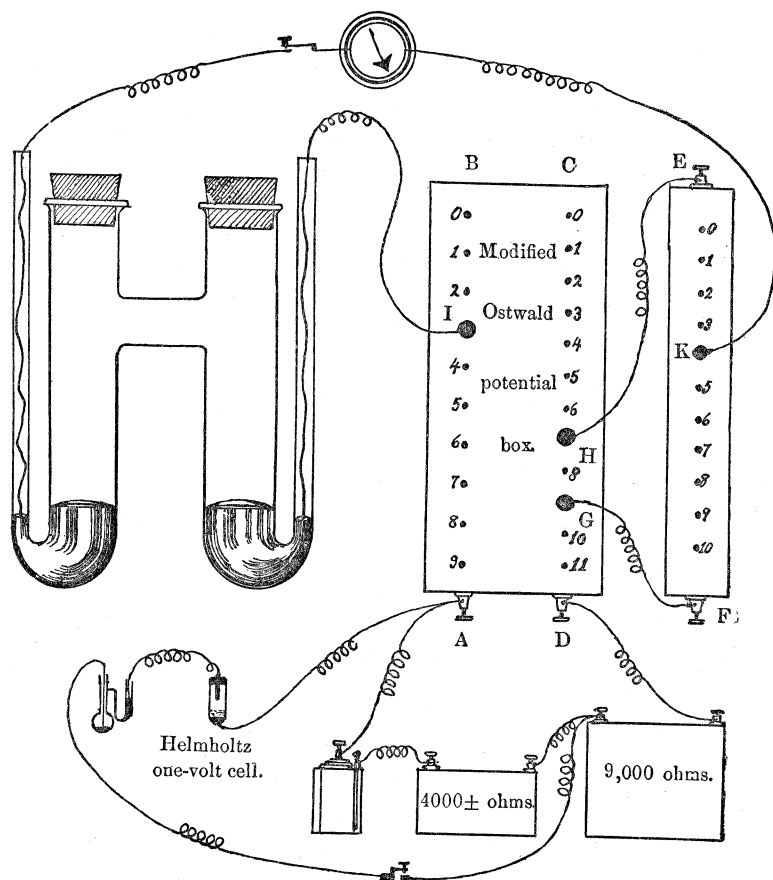
DIAGRAM OF APPARATUS.

The glass part at the left of the diagram is drawn about one third of the actual
size. The remainder of the apparatus is not drawn to scale, being annexed
merely to show the connections. For explanation, see page 91.

The cell was immersed in a thermostat which could be maintained
constant at any desired temperature within one tenth of a degree.

The electromotive forces were measured by means of an astatic gal-
vanometer according to the Poggendorff method. An Ostwald * "poten-
tial box," the resistances of which were carefully verified, was connected

* Ostwald, Hand- und Hilfsbuch, p. 252.

with a Leclanché cell through such external resistance as to maintain a total fall of potential of 0.1 volt. This was adjusted before each series of measurements by comparison with a standardized Helmholtz cell which remained constant in potential throughout the course of the experiments.

The direct measurement of potential as far as three figures when desirable was made possible by a device, the principle of which is shown in the accompanying diagram. AF represents a potential box containing three sets of resistances: AB, 9 times 100 ohms; CD, 11 times 10 ohms; EF, 10 times 2 ohms. These resistances are fitted with pegs for connection as in the ordinary potential box. $ABCD$ forms a simple circuit between the terminals A and D. EF is a shunt whose terminals can be connected with movable caps to the pegs in the row CD. If they are connected to two pegs, G and H, for example, between which there is 20 ohms resistance, the current between the pegs is evenly divided by the shunt. Thus arranged the total resistance of $C–D$ is 100 ohms, that of $A–B$ is 900 ohms, making 1,000 ohms for the whole box. A definite potential is maintained between A and D. If for example this is 0.1 volt, then the fall between two adjacent pegs is in AB 0.01 volt; in CD 0.001 volt (except between G and H, where the total fall is 0.001 volt); in EF 0.0001 volt. The cell, P, whose potential is to be measured, is connected through the galvanometer to the box by means of the caps I and K. Its potential is compensated, and there is no current through the galvanometer when it is equal to the total fall from B to I, from C to H, and from E to K. This value can be read directly from the box; thus the arrangement in the figure indicates a potential of 0.0374 volts. Of course even the next decimal place may be estimated from the deflections of the galvanometer when two adjacent pegs in EF on each side of the true point are connected in succession, or might be measured directly by yet another shunt similar to EF, with a total resistance of four ohms. In this case EF must be provided with an extra peg.

The external resistance of 13,000 ohms was calibrated during the course of the experiments. Owing to an error found in this box, it was necessary to correct the direct readings of potential of some of the early cadmium amalgam cells by multiplying with a constant factor. The corrected readings are given below without comment.

RESULTS.

Four classes of cells were studied: — (1) electrodes of cadmium amalgam of different concentration; (2) electrodes of zinc amalgam of

different concentration; (3) solid cadmium electrode opposed to cadmium amalgam; (4) solid zinc electrode opposed to zinc amalgam.

Class 1.

Table I. gives the values found for the electromotive forces of cells with electrodes of cadmium amalgams of different concentration. The lower extremity of each arm of the H tube was filled with amalgam to a depth of two or three centimeters, so that a fairly large volume might be present. Measurements were made at such temperatures that the amalgams were wholly liquid, for their partial solidification is an insidious cause of error capable of producing serious results, especially in this case of cadmium. The three per cent amalgam begins to freeze at about $0°$, becoming wholly solid at a slightly lower temperature (about —3°); while the nine per cent amalgam is not wholly liquid until 45° is reached. For this reason measurements 10 in Table I. had to be made at high temperatures. Normal cadmic sulphate was the electrolyte.

TABLE I. CADMIUM AMALGAMS.

	c_1	c_2	$\frac{c_1}{c_2}$	t	E (Obs.)	E (Calc.)	$\frac{E}{T}$
1	$\frac{1}{27}$	$\frac{1}{81}$	3	30	.01470	.0143	.0000485
2	$\frac{1}{9}$	$\frac{1}{27}$	3	30	.01470	.0143	.0000485
3	$\frac{1}{3}$	$\frac{1}{9}$	3	30	.01460	.0143	.0000482
				0	.01320	.0129	.0000483
4	$\frac{1}{3}$	$\frac{1}{9}$	3	30	.01445	.0143	.0000477
				0	.01303	.0129	.0000477
5	1	$\frac{1}{3}$	3	30	.01460	.0143	.0000482
				0	.01313	.0129	.0000481
6	1	$\frac{1}{3}$	3	30	.01450	.0143	.0000479
				0	.01313	.0129	.0000481
7	1	$\frac{1}{3}$	3	30	.01450	.0143	.0000479
				0	.01306	.0129	.0000478
8	1	$\frac{1}{3}$	3	30	.01450	.0143	.0000479
				0	.01306	.0129	.0000478
9	3	1	3	30	.01470	.0143	.0000485
10	9	3	3	72	.01993	.0163	.0000578
				60	.01915	.0157	.0000575

In the table, c_1 and c_2 represent the percentage by weight of cadmium in the amalgam, which in the case of dilute amalgams is proportional to the concentration by volume; t is the Centigrade temperature. The columns under E give the observed electromotive forces and those calculated from equation (2).

It was noticed by Meyer that the electromotive force of a cell of this kind increases rapidly upon standing. A similar effect was noticed by Jaeger[*] with solid cadmium amalgams. Although no explanation can be given of this phenomenon, one may prevent it by using as electrolyte a solution which has remained standing in contact with cadmium amalgam for several weeks before being used. The constancy thus reached permits much greater accuracy than could otherwise be obtained.

A study of the data of Table I. shows that the behavior of the last cell containing nine per cent amalgam differs materially from the rest. Regarding the electromotive forces of the other cells, it is to be noticed that, (1) at the same temperature they are all equal within limits of .0003 volt, therefore the potential depends on the ratio of c_1 to c_2, and not on their absolute values; (2) they are proportional to the absolute temperature; (3) they are uniformly higher than the values calculated from the formula, ranging from one per cent to three per cent too high. In the first two respects the amalgams obey rigidly the laws of dilute solutions. The small apparent deviation from these laws, indicated by the difference between the observed and calculated values, is therefore probably not a real deviation, but the effect of some slight side reaction in the cell.

The wide departure in the case of the last cell, on the other hand, shows that in amalgams of concentration as great as nine per cent there is a considerable deviation from the laws of dilute solution.

Theoretically, the nature of the anion of the electrolyte or the concentration of the kation should be without effect upon the result. This

TABLE II. VARYING ELECTROLYTES.

	c_1	c_2	t	E
$CdSO_4$ $\left(\frac{n}{1}\right)$ . . .	1	$\frac{1}{9}$	30	.02925
$CdSO_4$ $\left(\frac{n}{10}\right)$ . . .	1	$\frac{1}{9}$	30	.02915
CdI_2 $\left(\frac{n}{1}\right)$	1	$\frac{1}{9}$	30	.02920

[*] Wied. Ann., LXV. 106, 1898.

prediction was verified by experiment. Three similar cells were set up with different electrolytes, (1) normal cadmium sulphate, (2) tenth normal cadmium sulphate, (3) normal cadmium iodide. The results are shown in Table II. Theory demands 0.0286 instead of 0.0292.

Class 2.

The cells with electrodes of zinc amalgams were less constant in potential than those with cadmium, and the measurements were less trustworthy. Table III. gives the results with four cells of this type. The remarks on the preceding case apply here.

TABLE III. ZINC AMALGAMS.

	c_1	c_2	$\dfrac{c_1}{c_2}$	t	E (Obs.)	E (Calc.)	$\dfrac{E}{T}$
1	1	$\frac{1}{9}$	9	30	.02890	.0286	.0000954
				0	.02610	.0258	.0000956
2	$\frac{1}{3}$	$\frac{1}{27}$	9	30	.02920	.0286	.0000964
				0	.02625	.0258	.0000965
3	$\frac{1}{3}$	$\frac{1}{9}$	3	30	.01425	.0143	.0000470
				0	.01280	.0129	.0000469
4	$\frac{1}{9}$	$\frac{1}{27}$	3	30	.01515	.0143	.0000500
				0	.01365	.0129	.0000500

Class 3.

The measurement of the contact-potential of solid electrodes has always been subject to considerable uncertainty, due to accidents of crystallization, condition of surface, polarization, and other unknown causes. It seemed possible that by sufficiently increasing the extent and diversity of the surface an electrode might be obtained whose potential would be the mean of a large number of different values, and therefore constant. An electrode consisting of a quantity of finely divided metal perhaps a centimeter in depth, packed loosely around a sealed-in platinum wire seemed likely to satisfy the necessary conditions most nearly, and experiments made with zinc and cadmium electrodes of this sort yielded remarkably satisfactory results.

In order to justify the use of this solid electrode one must show that it always gives the same potential, and that this is equal to the true potential existing between metal and solution.   The first experiments were made with a cell whose electrolyte was cadmium sulphate and whose electrodes consisted of electrolyzed cadmium, of medium fineness, which had been washed successively in dilute sulphuric acid, distilled water, and absolute alcohol, and then dried.   The two electrodes being exactly similar, the electromotive force of the cell should be zero.   The actual electromotive force, therefore, indicates the amount of deviation in potential of electrodes of this kind.   Several such cells were measured. The largest electromotive force found was .0004 volt, the majority being about .0001 to .0002 volt.   Better results were obtained with metal which, instead of being dried, was washed in the electrolyte.   The difference of potential under these circumstances never exceeded .0001 volt when proper care was used in preparation.   Moreover no greater difference was found when two electrodes made of entirely different samples of electrolyzed cadmium were used.   Since, therefore, the same potential is obtained from such electrodes, whether the metal be in a finely divided spongy state, or consist of a coarser network of crystals, this may safely be considered the true potential of metallic cadmium.   Similar experiments were made with zinc, with equally satisfactory results.   The data given below illustrate the constancy of these electrodes.   The electrodes were usually not tested for any considerable length of time, the cells being prepared anew for each series of observations, which only lasted a few hours.   Table IV. gives the electromotive forces of cells where finely divided metallic cadmium was thus pitted against a dilute cadmium amalgam containing one per cent of cadmium.

TABLE IV. Cadmium versus Amalgam.

	E at 0°	E at 24.45°
Cell No. 1 . . .	0.06835	0.07345
Cell No. 2 . . .	0.06830	0.07345
Cell No. 3 . . .	0.06845	0.07360
Cell No. 4 . . .	0.06835	0.07350
Average . . .	0.06836	0.07350

On referring to equation (4),

$$E = KT + h,$$

it is obvious that we have here data for calculating h; for

$$K = \frac{dE}{dT}, = \frac{0.07350 - 0.06836}{24.45} = 0.0002102.$$

Upon this basis, $h = 0.01096$. But according to our original definition $h = \frac{Q}{ne_0}$, or $Q = hne_0$. In this case $n = 2$, and $e_0 = 23040$, expressed in such units that if E is in volts, $e_0 E$ will be in gram calories. Hence we have

$$Q = +505 \text{ small calories.}$$

This result represents the small quantity of heat given off when one gram atom (or 112.3 grams) of cadmium is dissolved in 11,100 grams of mercury. The constancy of the quotient in the last column of Table I. shows that further dilution does not increase this heat evolution.

Class 4.

A further application of equation (4) is presented in Tables V. and VI., which give the electromotive forces of cells whose electrodes were of zinc and one per cent zinc amalgam. The cells were kept at each temperature for ten minutes after constancy was reached.

Between the observations (4) and (5) in Table V. the thermostat was raised to higher temperatures, but above 37° hydrogen bubbles were evolved at the solid electrodes and the electromotive force became inconstant. The thermostat was then cooled to 34.5° and the electrodes were stirred and shaken to drive off the accumulated hydrogen. The readings were then resumed.

In Table VI. between observations (7) and (8) forty-eight hours intervened; so that the later results are not so trustworthy as the earlier ones. These observations are not used in the calculation, but are given merely in order to show that even a long immersion in the electrolyte does not seem to affect very greatly the condition of the spongy zinc.

The equation, based upon the starred observations in Table V., is as follows : —

$$E = 0.0002000 \, T - 0.04895.$$

Everywhere between 0° and 36° the values found agree almost exactly with the values calculated from this formula.

Here, as before, $Q = hne_0$; $n = 2$; $e_0 = 23040$; but in this case

$h = -.04895$. Therefore $Q = -2255$. That is, a gram atom of zinc (65.4 grams) takes up 2255 gram calories in dissolving in 6500 grams of mercury, or to greater dilution.

This method of determining thermal quantities is evidently one of great accuracy and convenience in cases where it is applicable. The data concerning the heats of amalgamation of zinc and cadmium which have previously been obtained are meagre. With these, however, the present results are in agreement. Thus Obach* found a cooling effect when zinc was amalgamated, a warming when cadmium was amalgamated. Favre † found for the heat of solution of amalgamated zinc 39.43 Kg-cal., for that of pure zinc 37.34 Kg-cal. The difference between the two represents the heat of amalgamation of zinc or —2100g-cal. The agreement of our result —2255 with this is striking.

The difference in potential between the solid metal and its saturated amalgam should be emphasized. It is often stated that the potential of

TABLE V. ZINC VERSUS AMALGAM.

	t	E (Obs.)		E (Calc.)
		(a)	(b)	
1	30.0	.01175	.01160	.01165
2	0.0	.00570‡	.00560‡	.00565‡
3	30.0	.01170‡	.01160‡	.01165‡
4	36.2	.01285		.01289
5	34.5	.01270	.01260	.01255
6	32.6	.01230	.01215	.01217
7	30.0	.01170	.01160	.01165
8	28.0	.01125	.01120	.01125
9	26.6	.01095	.01085	.01097
10	26.7	.01100	.01085	.01099
11	23.8	.01045	.01030	.01041
12	15.7	.00885	.00870	.00879
13	16.0	.00890	.00875	.00885

* Jahn, Grundriss der Elektrochemie, p. 8.   † Ibid.

‡ These values were taken as the basis of the formula.

TABLE VI. Zinc versus Amalgam.

	t	E (Obs.)		E (Calc.)
		(c)	(d)	
1	26.0	.01075	.01075	.01085
2	25.7	.01070	.01080	.01079
3	0.0	.00580	.00595	.00565
4	25.3	.01060	.01085	.01071
5	25.4	.01065	.01085	.01073
6	21.5	.00985	.01010	.00995
7	19.4	.00960	.00980	.00953
8	24.2	.01080	.01080	.01049
9	24.4	.01080	.01080	.01053
10	0.0	.00600	.00600	.00565
11	24.5	.01080	.01085	.01055
12	0.0	.00595	.00605	.00565
13	24.8	.01080	.01100	.01061

a saturated amalgam may be considered the potential of the pure metal. In the case of zinc this is true within a few thousandths of a volt; in the case of cadmium the difference between the solid metal and the saturated amalgam is 0.45 volt at 30°, and .054 volt at 0°.

SUMMARY.

The main points of the present paper may be summarized as follows : —

(1) A convenient method of measuring electromotive force directly to any desired number of decimal places is described.

(2) Cadmium amalgams as far as concentrations of three per cent and zinc amalgams to concentrations of at least one per cent obey closely the laws of dilute solution.

(3) The use of the Helmholtz equation for the temperature coefficient of a cell offers in these cases an accurate method of determining thermal quantities.

(4) The heat of amalgamation of cadmium is thus found to be +505 gram calories.

(5) The heat of amalgamation of zinc as thus found is —2255 gram calories.

(6) A solid electrode composed of finely divided electrolyzed metal gives a very constant and reliable potential.

(7) In the case of cadmium the contact-potential given by the saturated amalgam in reversible relation to an electrolyte differs by the twentieth of a volt from that given by the metal.

(8) In the case of zinc this difference is very slight.

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